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YALE UNIV NEW HAVEN CONN DEPT OF ENGINEERING AND AP--ETC F/6 7/4  
RAMAN CAPABILITIES FOR AEROSOL CHARACTERIZATION.(U)  
NOV 80 R K CHANG

DAA629-79-6-000R

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ARO-15030.6-GS

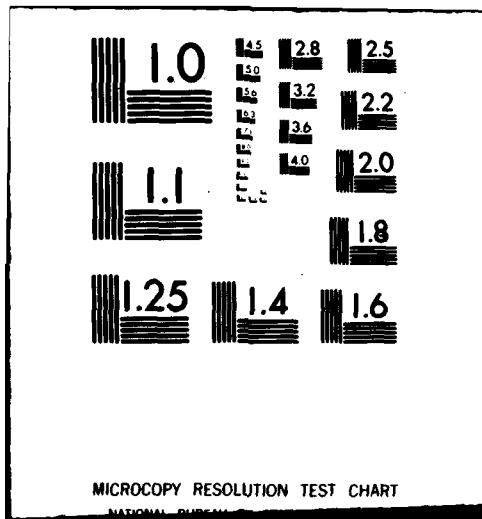
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**LEVEL 1**

9 **FINAL REPORT.**  
1 Oct 78-34 SEP 80,  
Submitted to the

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JAN 12 1981  
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U. S. Army Research Office

6 **RAMAN CAPABILITIES FOR AEROSOL CHARACTERIZATION.**  
15  
Grant No. DAAG29-79-G-0008

October 1, 1978 - September 30, 1980

12 13

10 Richard K. Chang  
Principal Investigator

11 November 1980

DEPARTMENT OF ENGINEERING  
AND APPLIED SCIENCE

YALE UNIVERSITY

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### OBJECTIVES OF THE RESEARCH PROJECT

Chemical speciation of microparticles can be achieved by spectral and intensity analyses of the inelastically scattered radiation (Raman and fluorescence). However, quantitative results by purely optical methods are intimately related to the environment with which the particles are in contact and the morphology of the microstructures. Morphology characterization of regularly shaped microparticles (spheres, cylinders, and spheroids) can be obtained by measuring the peaks in the extinction and elastically scattering spectra. Our investigation on the viability of quantitative species identification of molecules within a microparticle by inelastic laser scattering involved studies of the following: (1) dielectric and metal substrate interface to increase the intensity of the scattered radiation; and (2) morphology dependent dielectric resonances which can modify the scattering spectra.

### SUMMARY OF MAJOR RESULTS

The laser radiation used to induce inelastic scattering of the molecules contained within the microparticles (Raman or fluorescence scattering) usually also induces severe heating of the microparticle. Consequently, the particles are generally placed on a dielectric or metallic substrate for the purpose of conducting the laser induced heat away. We have been able to demonstrate that the dielectric or metallic substrate can actually be used to increase the coupling efficiency of the incident radiation into the microparticles as well as the scattered radiation out of the microparticles (publications 1, 2, and 3). For

the dielectric substrate, the attenuated total reflection technique involving a hemicylindrical prism is used to couple the incident radiation into and the scattered radiation out of the microparticles. For the metallic substrate, the surface plasmon polariton technique involving a thin Ag film overcoating on the hemicylindrical prism is used to couple the incident radiation into and the scattered radiation out of the microparticles. Increased intensity of the inelastic radiation by 10-100 x was achieved, as well as decreased angular spreading of the scattered radiation. Consequently, using the same incident laser power, we achieved overall improvement of the signal-to-noise ratio of the inelastically scattered radiation from various types of molecules embedded within the microparticles.

The angular distribution of the inelastic radiation (Raman and fluorescence) from microspheres is vastly different from the characteristic Lorenz/Mie elastic scattering, which is known to exhibit peaks and valleys as a function of angle relative to the incident beam direction. The angular pattern of the inelastic radiation was found to be smooth (publications 3 and 4). However, the exact shape of the angular pattern depended on the radius of the microspheres, as well as on the relative refractive index of the particle and the surrounding medium. Particular attention was paid to the backward-to-forward scattering intensity dissymmetry because of the importance of this parameter in remote chemical probing programs which use laser Raman radar techniques.

The intensities of the inelastic spectral peaks, measured at a fixed observation angle, are directly related to the concentrations

of different types of molecules. However, the intensity at specific wavelengths can be greatly enhanced as a result of the morphology of the microparticle, e.g., spheres, cubes, cylinders, and prolate/oblate spheroids. Artificial peaks can exist in the inelastic spectra from microparticles even though there are no such peaks in those spectra from large samples which are compositionally identical to the microparticles. We have found that a sharp increase in the Raman or fluorescence intensity will result when the inelastically scattered frequencies are resonant to the natural modes of oscillation of a microsphere or a fiber (publications 4 and 5). These natural modes of oscillation are commonly called morphology defined structure resonances.

Morphology defined structure resonances can also be excited by the incident radiation. When the incident frequencies are resonant to these natural modes of oscillation of the microstructures, large increases in the elastically scattered intensity result. We have shown experimentally that, by monitoring the peaks in the elastically scattered intensity as a function of incident wavelength, morphology characterization can be achieved for infinitely long fibers (publication 6). For optical fibers, in particular, we have devised a totally new technique of ultra-precise diameter sizing as the fiber is being pulled from the preform.

Morphology defined structure resonances can also exist in metallic microparticles (e.g., Ag, Au, and Cu colloids and wires). The structure resonances of metallic micro-objects are associated with surface plasmons, which are much less sensitive to particle size and shape than are the dielectric surface electromagnetic waves. Extremely large extinction,



elastic scattering, and absorption can result when the incident photon energy is capable of exciting the surface plasmon resonances. Thus, the study of surface plasmon resonances in microparticles is directly related to the Army's obscuration program which requires large extinction at specific incident wavelengths. We have calculated the wavelength and radius dependences of the extinction, elastic scattering, absorption, and near-field intensity at the interface of Ag, Au, and Cu spheres (publication 7). A close connection exists between surface plasmon resonances and the recently discovered giant surface enhancement ( $10^5$ - $10^6$  x) of the Raman scattering from molecules adsorbed on the metallic colloids, electrodes, and thin films. The latter topic can have application to electrochemistry and catalysis.

We believe the most important contribution resulting from our two years of ARO support is the formation of an effective experimental program. Our new results have been used to critically test existing theories and calculations, as well as to stimulate new theoretical models for physical processes in light interactions with microparticles. By using dielectric and metallic interfaces, we have been able to increase the signal-to-noise ratio of the inelastic scattering which provides unique information on the chemical species contained within the microparticles. We have shown experimentally that morphology defined resonances exist in dielectric as well as metallic micro-objects. These resonances give rise to enhanced extinction, elastic and inelastic scattering, and absorption and also provide a new technique for the characterization of microparticles.

## PUBLICATIONS\*

1. R. E. Benner, R. Dornhaus, M. B. Long, and R. K. Chang, "Inelastic Light Scattering from a Distribution of Microparticles," Microbeam Analysis 1979, Proceedings of the 14th Annual Conference of the Microbeam Analysis Society, edited by Dale E. Newbury (San Francisco Press, San Francisco, 1979), p. 191.
2. R. E. Benner, R. Dornhaus, and R. K. Chang, "Angular Emission Profiles of Dye Molecules Excited by Surface Plasmon Waves at a Metal Surface," Opt. Commun. 30, 145 (1979).
3. R. E. Benner, J. F. Owen, and R. K. Chang, "Radiation Patterns of Inelastic Reemission from Microparticles in Homogeneous Surroundings and near Dielectric or Metal Interfaces," J. Phys. Chem. 84, 1602 (1980).
4. R. K. Chang, J. F. Owen, P. W. Barber, B. J. Messinger, and R. E. Benner, "Inelastic Light Emission from Spherical Particles and Cylindrical Fibers," J. Raman Spectrosc. (in press).
5. R. E. Benner, P. W. Barber, J. F. Owen, and R. K. Chang, "Observation of Structure Resonances in the Fluorescence Spectra from Microspheres," Phys. Rev. Lett. 44, 475 (1980).
6. J. F. Owen, P. W. Barber, B. J. Messinger, and R. K. Chang, "Determination of Optical Fiber Diameter from Resonances in the Elastic Scattering Spectrum," submitted to Opt. Lett.
7. B. J. Messinger, K. U. von Raben, R. K. Chang, and P. W. Barber, "Local Fields at the Surface of Noble Metal Microspheres," submitted to Phys. Rev.

\* Reprints of all published papers have been submitted to ARO.

PARTICIPATING SCIENTIFIC PERSONNEL

- Robert E. Benner - Postdoctoral Fellow.  
Promoted to Assistant Professor, Yale  
Department of Engineering and Applied Science.  
  
Present address: Sandia Laboratories  
Livermore, CA 94550
- Ralf Dornhaus - Postdoctoral Fellow.  
  
Present address:  
I. Physikalisches Institut der RWTH Aachen  
5100 Aachen 1, West Germany
- Marshall B. Long - Graduate student.  
Promoted to Acting Instructor.  
Promoted to Assistant Professor, Yale  
Department of Engineering and Applied Science
- James F. Owen - Postdoctoral Fellow.  
Promoted to Lecturer, Yale  
Department of Engineering and Applied Science.
- Carla Escoda - Yale senior.  
Worked on the ARO project the summer of  
1980 prior to entering graduate school  
in the Yale Department of Engineering  
and Applied Science.
- Barbara Messinger - M.I.T. senior.  
Her senior project related to the ARO  
research topic was done at Yale.
- Peter W. Barber - Associate Professor, University of Utah.  
Spent a one-year sabbatical working on  
the ARO research topic at Yale.

WORKSHOPS HELD AT YALE ON LIGHT SCATTERING FROM SMALL PARTICLES

December 14-15, 1978

Topics:

1. Theory of morphology defined dielectric resonances (P. Chýlek, G. J. Rosasco, and M. Kerker).
2. Optical levitation of microspheres (A. Ashkin).
3. Calculations on nonspherical particle scattering (P. W. Barber and D.-S. Wang).
4. Experiments and theory of light scattering from spherical particles (R. K. Chang, R. E. Benner, M. Kerker, P. J. McNulty, and H. Chew).
5. Experiments and theory of light scattering from particles on or near an interface (R. K. Chang, R. E. Benner, and H. Chew).

December 19-20, 1979

Topics:

1. Theory and experiments of morphology defined dielectric resonances (E. K. Miller, A. Ashkin, R. E. Benner, R. K. Chang, P. W. Barber, and J. F. Embury).
2. Nonspherical particles (P. W. Barber, R. F. Harrington, M. Kerker, S. K. Chang, and P. J. McNulty).
3. Metallic particles (A. J. Sievers and R. P. Andres).
4. Inelastic emission (M. Kerker, G. J. Rosasco, H. Chew, E. S. Etz, S. Arnold, and R. K. Chang).

PRESENTATIONS AT CSL SCIENTIFIC CONFERENCES  
ON OBSCURATION AND AEROSOL RESEARCH  
(organized by E. Stuebing)

September 17-21, 1979

"Intensity and Angular Pattern of the Inelastic Radiation from Monodispersed Spherical Aerosols."

July 21-25, 1980

"Resonances Structures in Fluorescence and Raman Spectra from Microspheres: A Sensitive Measure of Particle Diameter."

"Elastic and Inelastic Light Scattering from Optical Fibers: Radiation Patterns and Particle Morphology."

VISIT TO ARMY LABORATORY  
(organized by R. Pinnick)

August 17, 1979

Visited U. S. Army Electronics Research and Development Command, Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A093704	
4. TITLE (and Subtitle)		5. TYPE OF REPORT & PERIOD COVERED
RAMAN CAPABILITIES FOR AEROSOL CHARACTERIZATION		Final 10/1/78 - 9/30/80
7. AUTHOR(s)		6. PERFORMING ORG. REPORT NUMBER
Richard K. Chang		
9. PERFORMING ORGANIZATION NAME AND ADDRESS		8. CONTRACT OR GRANT NUMBER(s)
Yale University Department of Engineering and Applied Science New Haven, CT 06520		DAAG29-79-G-0008
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		15030-GS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE
		November 1980
		13. NUMBER OF PAGES
		10
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
NA		
18. SUPPLEMENTARY NOTES		
The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Microparticle chemical analysis      Microspheres Morphology characterization      Optical fibers Scattering      Surface plasmon polaritons Raman effect      Attenuated total reflection Fluorescence		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Chemical speciation of microparticles can be achieved by spectral analysis of inelastically scattered radiation. Microparticle morphology and substrate contact with the microparticle affect the spectral content. Dielectric and metallic substrate interfaces have been used to increase the inelastic intensity. Morphology defined resonances in microparticles have been studied in detail as another means of increasing the inelastic intensity. The artificial peaks which can occur in dielectric microparticles as a result of the morphology defined resonances have also been investigated both theoretically and experimentally.		

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